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(21) International Application Number: PCT/DK94/00238 (22) International Filing Date: 16 June 1994 (16.06.94) (30) Priority Data: 0722/93 18 June 1993 (18.06.93) DK 08/136,459 15 October 1993 (15.10.93) US (71) Applicant (for all designated States except US): DANPREN A/S [DK/DK]; 15 Roholmsvej, DK-2620 Albertslund (DK). (72) Inventors; and (75) Inventors/Applicants (for US only): GRENNES, Torbjørn [DK/DK]; 102 Breeteparken, DK-2970 Hørsholm (DK). NIELSEN, Bent [DK/DK]; 65 Duevej, DK-2000 Frederiksberg (DK). (74) Agents: SCHØNNING, Søren et al.; Internationalt Patent-Bureau, 23 Høje Taastrup Boulevard, DK-2630 Taastrup (DK).		(81) Designated States: AT, AU, BB, BG, BR, BY, CA, CH, CN, CZ, DE, DK, ES, FI, GB, GE, HU, JP, KE, KG, KP, KR, KZ, LK, LU, LV, MD, MG, MN, MW, NL, NO, NZ, PL, PT, RO, RU, SD, SE, SI, SK, TJ, TT, UA, US, UZ, VN, European patent (AT, BE, CH, DE, DK, ES, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG). Published With international search report.										
(54) Title: A THIN-WALLED RUBBER ARTICLE, PROCESS FOR THE PREPARATION OF THE RUBBER ARTICLE AND A SOLUTION FOR THE PREPARATION OF SAID RUBBER ARTICLE												
(57) Abstract <p>A thin-walled rubber article with a high tear resistance prepared by dip forming, comprising a polymer blend which comprises 10-75 % by weight styrene-isoprene-styrene (S-I-S) triblock copolymer, 1-90 % styrene-butadiene-styrene (S-B-S) triblock copolymer, and 0-25 % by weight styrene-olefin-styrene (S-O-S) triblock copolymer.</p> <div data-bbox="982 1144 1435 1957"><p>N/mm THICKNESS</p><table border="1"><caption>Tear Resistance Data (Estimated from Graph)</caption><thead><tr><th>% S-I-S</th><th>Tear Resistance (N/mm)</th></tr></thead><tbody><tr><td>10</td><td>~5</td></tr><tr><td>25</td><td>~8</td></tr><tr><td>50</td><td>~12</td></tr><tr><td>75</td><td>~52</td></tr></tbody></table><p>TEAR RESISTANCE STERILE</p></div>			% S-I-S	Tear Resistance (N/mm)	10	~5	25	~8	50	~12	75	~52
% S-I-S	Tear Resistance (N/mm)											
10	~5											
25	~8											
50	~12											
75	~52											

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A THIN-WALLED RUBBER ARTICLE, PROCESS FOR THE PREPARATION OF
THE RUBBER ARTICLE AND A SOLUTION FOR THE PREPARATION OF
SAID RUBBER ARTICLE

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Background of the invention

The present invention relates to a thin-walled rubber
article, such as for instance gloves or condoms, prepared by
10 dip forming. Moreover, the invention relates to a process for
the preparation of such rubber article and to a solution for
the preparation of said rubber article.

Soft, elastomeric, protective rubber articles, for
instance gloves or condoms, have for a long time been made
15 from natural latex or natural rubber dissolved in a suitable
solvent, for instance aliphatic hydrocarbons. In order to
obtain articles with a sufficiently high strength and ela-
sticity it is necessary to vulcanize or in other ways chemi-
cally cross-linking the molecule chains of the rubber, which
20 requires the presence of curing-agents, activators, accele-
rators, and possibly antioxidants. The presence of such
agents often give rise to allergic reactions among the users
of said articles.

Furthermore, all latices of natural rubber contains
25 proteins, which may cause type I allergy (immediate hyper-
sensitivity reaction) resulting in fatal cases in anaphylac-
tic chock.

Great efforts have therefore been made to develop
rubber articles based on synthetically manufactured rubber
30 types, which do not have the drawbacks of natural rubber.

Thus US Patents Nos. 3,933,723 and 5,112,900 both re-
late to solutions containing thermoplastic styrene-triblock
copolymers and a plasticizer for the production of rubber
articles. Common to the solutions disclosed in the two
35 above-mentioned patents is that by the formation of the
solid film a physical cross-linking takes place between the
block copolymer molecules present in the solution, when the
solvent evaporates, said cross-linking being caused by the

styrene domains of the molecular chains. Thereby the use of potentially allergy causing chemicals for the provision of a chemical cross-linking between the block copolymer molecules is avoided. Furthermore, these solutions do not contain the proteins present in natural rubber, and it is thus possible by using these solutions to prepare hypo-allergenic rubber articles.

The rubber articles disclosed in US Patent No. 3,933,723 have in comparison with the rubber articles according to US Patent No. 5,112,900 a higher tensile strength and elongation, in particular after radiation sterilization. Furthermore, they have a lower modulus and consequently a better tactility for the user. However, the tear resistance of the rubber articles disclosed in US Patent No. 3,933,723 is low, and it is desirable to improve this property in such a way that for instance a glove gets a higher mechanical stability when getting in contact with pointed articles.

The rubber articles disclosed in both the above-mentioned US patents contain in order to attain the desired mechanical properties comparatively large amounts of plasticizer, which is preferably consisted by a naphthenic or aromatic mineral oil.

Summary of the invention

It has surprisingly turned out to be possible to replace the entire part or the major part of the naphthenic or aromatic oil disclosed in US Patent No. 3,933,723 by a styrene-isoprene-styrene triblock copolymer (S-I-S triblock copolymer), thereby obtaining an unexpectedly high tear resistance. Besides, it has turned out that rubber articles in which the naphthenic or aromatic oil has been replaced by an S-I-S triblock copolymer, have an improved resistance towards yellowing and towards quick disintegration of the physical properties, when exposed to sunlight.

The object of the present invention, which is a further development of the subject matter disclosed in US Patent No. 3,933,723, is to provide a rubber article with high tensile strength and elongation even after radiation

sterilization and a low modulus, and which at the same time has an excellent tear resistance and good resistance towards the sunlight.

The object of the invention is met by providing a
5 thin-walled rubber article comprising a polymer blend which comprises

10-75% by weight styrene-isoprene-styrene (S-I-S)
triblock copolymer,

1-90% styrene-butadiene-styrene (S-B-S) triblock copolymer, and

0-25% by weight styrene-olefin-styrene (S-O-S) triblock copolymer.

Moreover, the invention relates to a process for the preparation of a thin-walled rubber article, said process
15 comprising the steps of:

a) dipping a form in a polymer blend comprising 10-75% by weight S-I-S triblock copolymer, 1-90% by weight S-B-S triblock copolymer, and 0-25% by weight S-O-S triblock copolymer, dissolved in an inert solvent substantially constituted by aliphatic hydrocarbons with a boiling point between
20 95° and 140°C in an amount, based on the polymer blend, of from 400 to 1200% by weight, said solution optionally comprising a naphthenic or an aromatic mineral oil as plasticizer in an amount up to about 30% by weight, based on the
25 polymer blend,

b) removing the form from the solution, and,

c) allowing the solvent to evaporate,

which process may be repeated, until the rubber article has attained the desired wall-thickness.

30 As solvent for the copolymer blend any inert solvent may be used, a solvent mainly consisting of aliphatic hydrocarbons being, however, preferred, as vapours from aliphatic hydrocarbons have lower toxicity than for instance halogen-containing or aromatic solvents. To obtain a sufficiently
35 good dissolution of the copolymer blend and good process properties the solvent may advantageously contain a smaller amount of aromatic compounds, for instance up to 10% by weight of the solvent mainly consisting of aliphatic hydro-

carbons may be aromatic compounds. It is furthermore preferable that the aliphatic hydrocarbons have a boiling point between 95°C and 140°C. Based on the blend of copolymers the amount of solvent preferably constitutes 400-1200% by weight.

The solution for the preparation of a rubber article according to the invention may contain more than one variant of each type of triblock copolymers to attain a desired viscosity of the solution and/or to attain the desired mechanical properties of the rubber article. By "more than one variant" is to be understood that the solution for each type of triblock copolymer may contain several variants of triblock copolymers with different styrene content and with different solution viscosity.

A triblock copolymer can, when the monomers, from which the blocks are built, are known, be unambiguously characterized by the viscosity of a predetermined concentration in a solvent and the content of the end blocks in the triblock copolymer. Thus a S-I-S triblock copolymer may unambiguously be characterized by its solution viscosity in a 25% by weight solution in toluene at a specified temperature and by its styrene content.

In the solution for the preparation of the rubber article according to the invention it is preferred to use a S-I-S triblock copolymer with a styrene content of from 10-30% by weight and a solution viscosity in a 25% by weight solution in toluene at 25°C of 0.5-5 Pa.s.

S-I-S triblock copolymers may for instance be of the type sold under the name Cariflex TR1107 or Cariflex TR1111, which has a styrene content of 15% and 22%, respectively, and a solution viscosity in a 25% by weight solution in toluene at 25°C of 1.6 and 1.4 Pa.s., respectively.

As S-B-S triblock copolymers, copolymers with a very varying solution viscosity may be used, for instance with a solution viscosity in a 25% by weight solution in toluene at 25°C of 0.5-30 Pa.s., but usually with a styrene content between 20 and 40% by weight. Examples of applicable S-B-S triblock copolymers, which may be used alone or in combina-

tion is: Cariflex TR1101 with a styrene content of 31% by weight and a solution viscosity in a 25% by weight solution in toluene at 25°C of 4.0 Pa.s. Cariflex TR1102 with a styrene content of 29% by weight and a solution viscosity in a 25% by weight solution in toluene of 1.2 Pa.s, and Cariflex 1184 with a styrene content of 30% by weight and a solution viscosity in a 25% by weight solution in toluene at 25° of 20.0 Pa.s.

If a rubber article is prepared from a solution containing solely S-I-S triblock copolymers, the rubber article gets a very low modulus, and the viscosity of the solution will be too low for the preparation of suited rubbers articles by dip forming, as the walls of the rubber articles will be too thin and sticky.

If a rubber article is prepared from a solution containing solely S-B-S triblock copolymers, the modulus of the article will be too high, the article thus getting insufficient elasticity.

As mentioned above it has hitherto only been possible to prepare thin-walled rubber articles with satisfactory mechanical properties on basis of S-B-S triblock copolymers by adding to the solution fairly large amounts of plasticizer, in the form of a naphthenic or aromatic mineral oil. It has now unexpectedly turned out to be possible to completely or partly replace the hitherto used plasticizers by S-I-S triblock copolymers.

In a preferred embodiment of the invention the previously used naphthenic or aromatic mineral oils are completely replaced by S-I-S triblock copolymers. The content of S-B-S triblock copolymer is from 1-90% by weight, in particular from 25-40% by weight of the blend of copolymers, and the remaining part is a S-I-S triblock copolymer. Preferably the blend of copolymers is constituted by about 1 part by weight S-B-S triblock copolymer and about 2 parts by weight S-I-S triblock copolymer. A thin-walled rubber article prepared from such a copolymer blend has, in addition to an excellent tear resistance, good resistance towards sunlight, but is somewhat sensitive to influence from ozone, as ozone

will react with double bonds which are present in polymerized butadiene.

In another preferred embodiment of the invention a rubber article with a greater ozone resistance is provided thereby that a part of the S-B-S triblock copolymer is replaced by styrene-olefin-styrene (S-O-S) triblock copolymers. The content of S-O-S in the polymer blend can for example be from 0 to 25% by weight. Polymerized olefin is saturated, i.e. contains no double bonds, and is therefore less sensitive towards ozone. Such a substitution may necessitate that the solvent, apart from aliphatic hydrocarbons, contains a smaller amount of aromatic hydrocarbons in order to attain an applicable solution and in order to secure the development of a polymer matrix in which the various polymer chains form an interpenetrating molecular network. Furthermore, the substitution may necessitate the presence of a smaller amount of naphthenic oil.

As S-O-S triblock copolymer styrene-ethylene/butylene-styrene (S-EB-S) triblock copolymers may for instance be used, preferably with a styrene content of 10-30% by weight and a solution viscosity in a 25% by weight solution in toluene at 25° of 1-10 Pa.s.

Preferably, the thin-walled rubber article according to the second embodiment comprises a polymer blend which comprises 10 to 25% by weight S-B-S triblock copolymer, 10 to 25% by weight S-EB-S triblock copolymer and 60 to 75% by weight S-I-S triblock copolymer. More preferable the rubber article comprises about one part S-B-S triblock copolymer, about one part S-EB-S triblock copolymer and about 4 parts S-I-S triblock copolymer. The rubber article comprising this copolymer blend preferably further contains up to about 30% by weight of a naphthenic or an aromatic mineral oil as plasticizer, based on the copolymer blend.

If desired, the solution for the production of thin-walled rubber articles may contain commonly used stabilizers and additives. Such a stabilizer might for instance be a zinc dithiocarbamate.

Other features and advantages of the invention will

be apparent from the following more detailed description of the preferred embodiments, taken in conjunction with the accompanying drawings, which illustrate, by way of example, the principles of the invention.

5

Brief description of the drawings

Fig. 1 shows modulus at an elongation of 500% of a not sterilized specimen, a sterilized specimen and a steril-
10 ized specimen aged for 7 days at 70°C.

Fig. 2 shows the tensile strength of a not sterilized sample, a sterilized specimen and a sterilized specimen aged for 7 days at 70°C.

Fig. 3 shows the elongation of a not sterilized specimen, a sterilized specimen and a sterilized specimen aged
15 for 7 days at 70°C.

Fig. 4 shows the tear resistance of a sterilized specimen, and

Fig. 5 shows the wall-thickness of the specimen.

20

Detailed description of the preferred embodiments

All the specimen are prepared by dipping a condom-shaped form in the solution described below and then slowly removing the form from the solution, a thin, uniform layer
25 of the solution thus adhering to the form. The form with the adhering amount of solution is then dried in an air current at room temperature to evaporate the solvent from the thin elastomeric layer. This process may be repeated until the rubber article has obtained the desired wall-thickness.

30 The solution is prepared by dissolving a copolymeric blend of S-I-S (Cariflex TR1111) and S-B-S (Cariflex TR1101) triblock copolymer in the amounts given in the abscissa in 850% by weight of a solvent consisting of aliphatic hydrocarbons with a boiling point from 95-140°C, and then adding
35 0.5% by weight of zinc dibutyl-dithiocarbamate, the statement of amounts being based on 100% by weight of the copolymers.

From Fig. 1 will be seen that an increased content of

the S-I-S-copolymer causes a considerable drop in modulus, but this has a surprisingly small effect on the tensile strength, see Fig. 2, which substantially remains constant. The elongation stated in Fig. 3 is increased in a way to be expected. The tear resistance stated in Fig. 4 is surprisingly increasing considerably by an increased content of the S-I-S-copolymer. From Fig. 5 will be seen that the thickness of the rubber article decreases by an increased content of the S-I-S-copolymer on account of the lower viscosity of the solution and the subsequent reduced adherence to the form. If comparing Fig. 5 with Fig. 1 the necessity of adding a softener in the form of mineral oil becomes apparent, when small amounts of S-I-S-copolymers in the solution are used, if it is the object to produce thin-walled articles with a low modulus and a subsequent good tactility, where a low tear resistance is acceptable.

From Fig. 3 will be seen that the degree of reduction of the quality on account of the necessary radiation sterilization normally is independent of the content of the S-I-S-copolymer. The same applies to the further reduction of the quality, which takes place in the aging test (7 days at 70°C). The reduction of the quality is, however, not so pronounced that the specimen do not comply with the present ASTM standard no. D3577-78 (1991).

Tests of the tear resistance of the various specimen are made on a dump bell specimen cut out of a rubber film with 8 mm between the parallel sides, in which an incision of 1 mm is made at the edge of one of the parallel sides. The tear resistance is then calculated as the ratio between the perpendicular force, which is to be applied to make the rubber film break, and the thickness of the film.

The invention being thus described, it will be obvious that the same may be varied in many ways. Such variations are not to be regarded as a departure from the spirit and scope of the invention, and all such modifications as would be obvious to one skilled in the art are intended to be included within the scope of the following claims.

What we claim is:

1. A thin-walled rubber article comprising a polymer blend which comprises
 - 5 10-75% by weight styrene-isoprene-styrene (S-I-S) triblock copolymer,
 - 1-90% styrene-butadiene-styrene (S-B-S) triblock copolymer, and
 - 0-25% by weight styrene-olefin-styrene (S-O-S) triblock copolymer.
2. A rubber article according to claim 1, wherein the polymer blend contains from 60 to 75% by weight S-I-S triblock copolymer and 25-40% by weight S-B-S triblock copolymer.
- 15 3. A rubber article according to claim 1, wherein the S-I-S triblock copolymer has a styrene content of from 10 to 30% by weight and a solution viscosity in a 25% by weight solution in toluene at 25°C of 0.5 - 5 Pa.s and the S-B-S triblock copolymer has a styrene content of from 20 to 40%
20 by weight and a solution viscosity in a 25% by weight solution in toluene at 25°C of 0.5 - 30 Pa.s.
4. A rubber article according to claims 1-3 further comprising a naphthenic or an aromatic mineral oil as plasticizer in an amount up to about 30% by weight, based on the
25 polymer blend.
5. A rubber article according to claims 1-4, wherein the styrene-olefin-styrene (S-O-S) triblock copolymer is styrene-ethylene/butylene-styrene (S-EB-S) triblock copolymer.
6. A thin-walled rubber article according to claims 1-5,
30 comprising a polymer blend which comprises
 - 60 - 75% by weight S-I-S triblock copolymer,
 - 10 - 25% by weight S-B-S triblock copolymer,
 - 10 - 25% by weight (S-EB-S) triblock copolymer, and
 - up to about 30% by weight of a naphthenic plasticizer, based on the copolymers.
- 35 7. A rubber article according to claims 5 and 6, wherein the S-EB-S triblock copolymer has a styrene content of from 10 to 30% by weight and a solution viscosity in a 25% by

weight solution in toluene at 25°C of a 1 - 10 Pa.s.

8. A process for preparing a thin-walled rubber article according to claims 1-7 comprising the steps of:

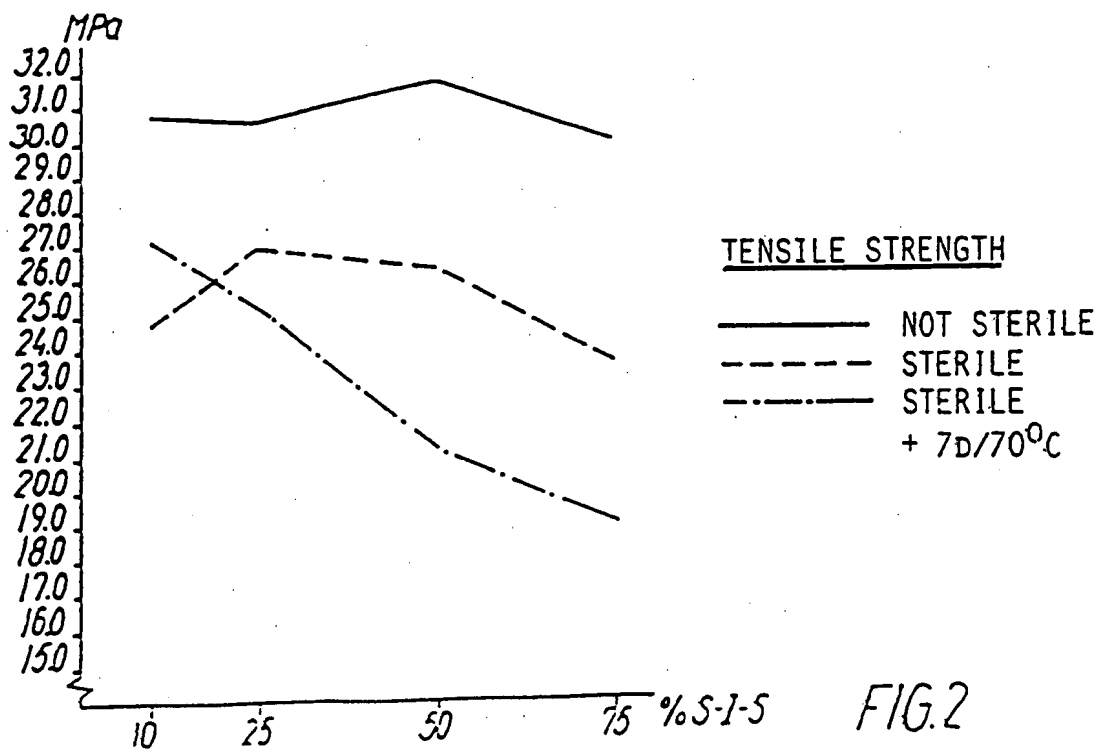
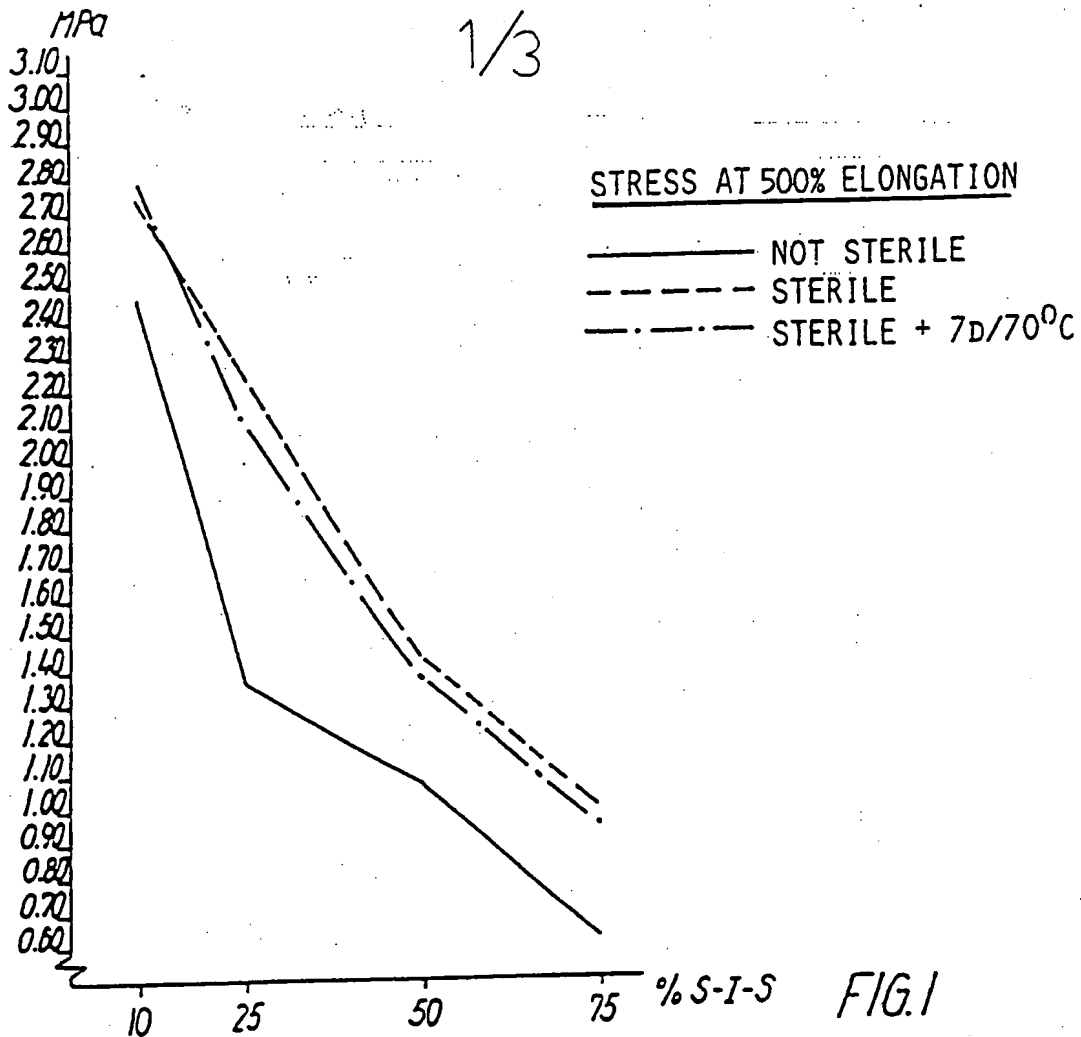
- (a) dipping a form in a polymer blend comprising 10-75%
5 by weight S-I-S triblock copolymer, 1-90% by weight S-B-S
triblock copolymer and 0-25% by weight S-O-S triblock copolymer, dissolved in an inert solvent substantially constituted by aliphatic hydrocarbons with a boiling point between
95° and 140°C in an amount, based on the polymer blend, of
10 from 400 to 1200% by weight, said solution optionally comprising a naphtenic or an aromatic mineral oil as plasticizer in an amount up to about 30% by weight, based on the polymer blend,
(b) removing the form from the solution, and
15 (c) allowing the solvent to evaporate,
which process may be repeated until the rubber article has attained the desired wall-thickness.

9. A process according to claim 8, wherein the blend of copolymers contains 60-75% by weight S-I-S triblock copolymer and 25-40% by weight S-B-S triblock copolymer.
20

10. A solution for the preparation of thin-walled rubber articles according to claims 1-7 by dip forming, comprising a polymer blend which comprises

60-75% by weight S-I-S triblock copolymer having a
25 styrene content of from 10 to 30% by weight and a solution viscosity in a 25% by weight solution in toluene at 25°C of 0.5 - 5 Pa.s, and

25-40% by weight S-B-S triblock copolymer having a
styrene content of from 20 to 40% by weight and a solution
30 viscosity in a 25% by weight solution in toluene at 25°C of 0.5 - 30 Pa.s,
dissolved in an inert solvent substantially consisting of aliphatic hydrocarbons, the solvent being present in an amount sufficient for forming a stable solution and for per-
35 mitting dip forming of rubber articles from the solution.



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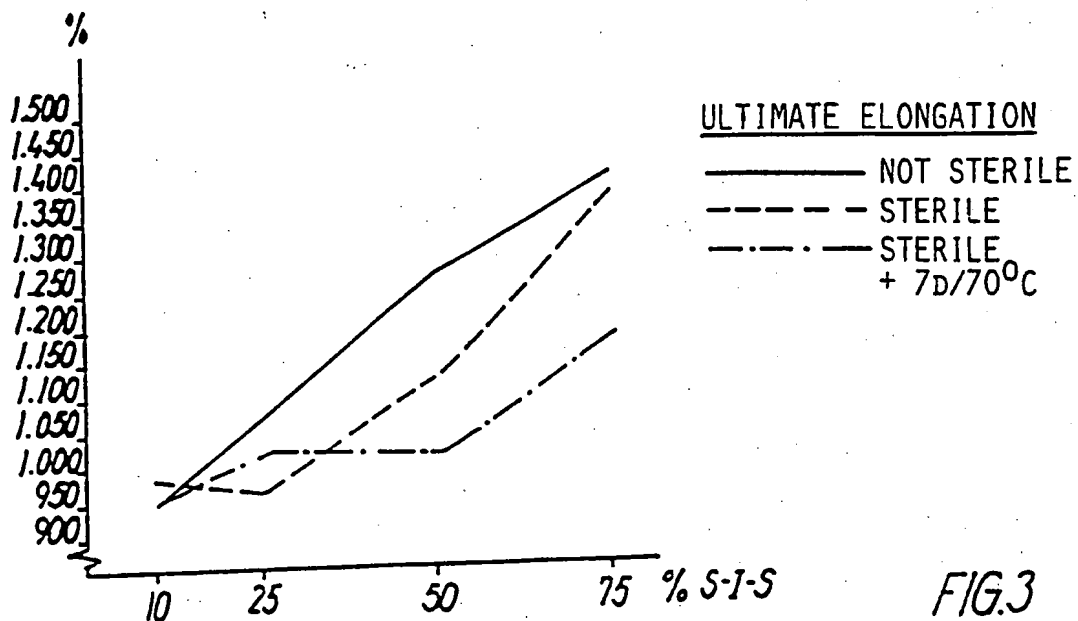


FIG.3

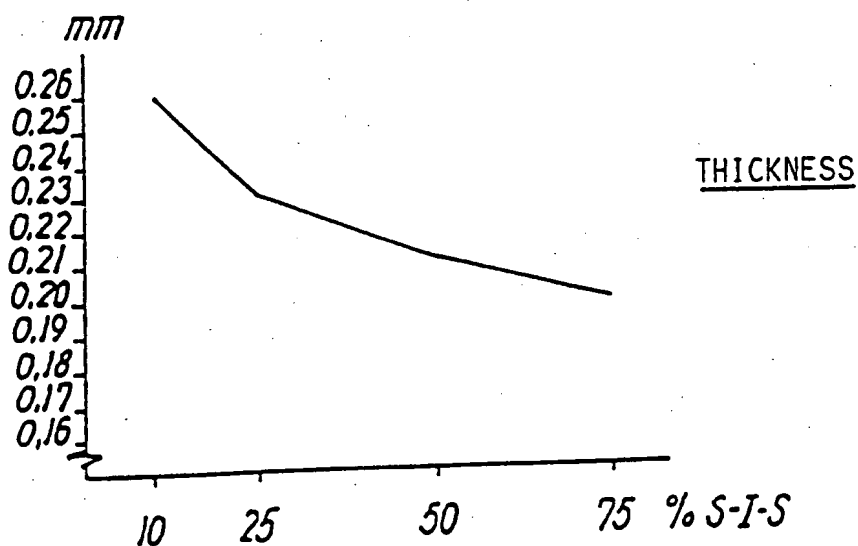
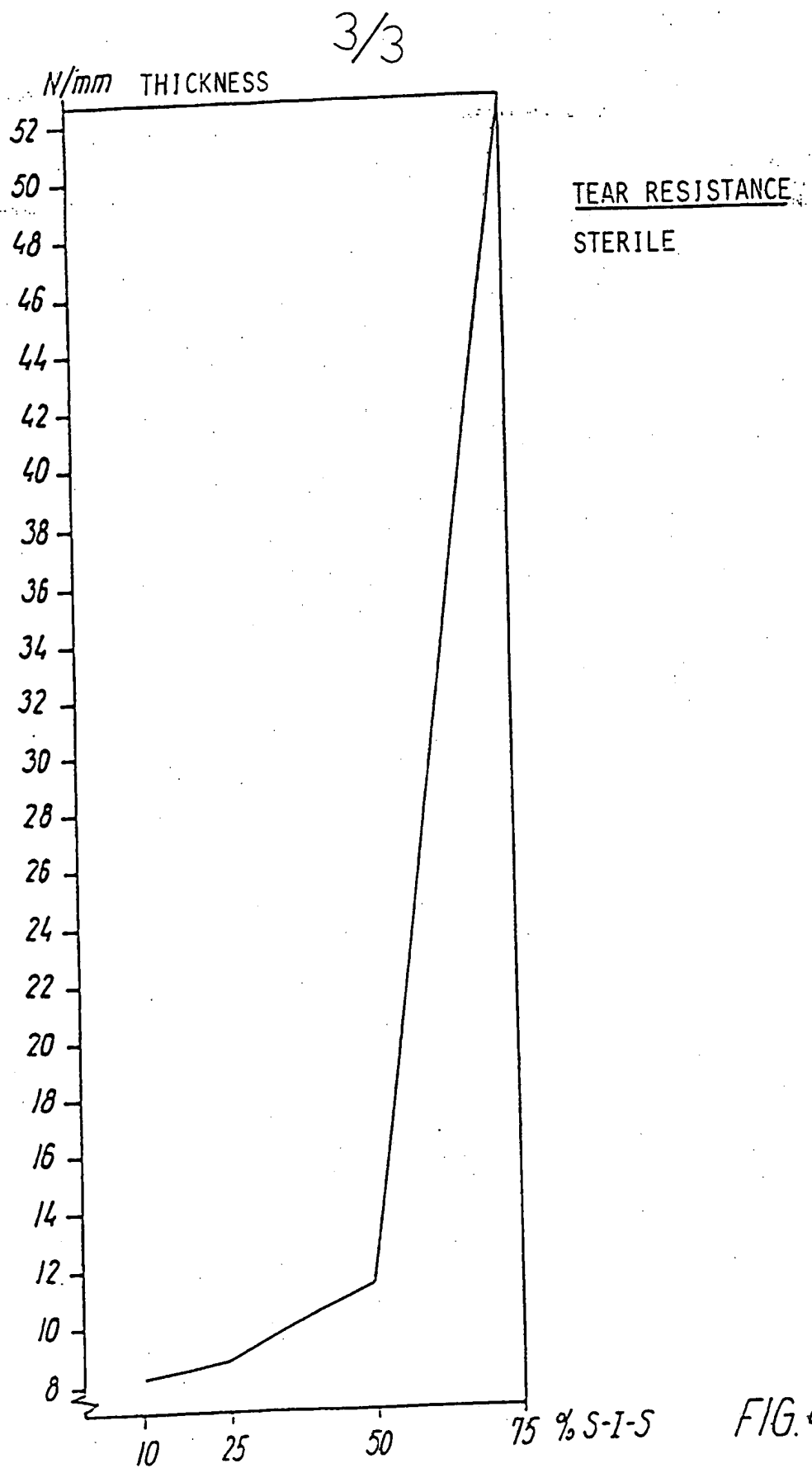


FIG.5



INTERNATIONAL SEARCH REPORT

International application No.

PCT/DK 94/00238

A. CLASSIFICATION OF SUBJECT MATTER

IPC⁵: C08L 9/06

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

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C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US, A, 5112900 (D.A. BUDDENHAGEN ET AL.), 12 May 1992 (12.05.92), claims 1-21 --	1-10
Y	Chemical Abstracts, Volume 94, No 22, 1 June 1981 (01.06.81), (Columbus, Ohio, USA), page 382, THE ABSTRACT No 180698f, JP, A, 8120515, (SUZUKI NIPPONDO CO., LTD.) 26 February 1981 (26.02.81) --	1-10
A	US, A, 3933723 (T. GRENNES), 20 January 1976 (20.01.76), the whole document -----	1-10

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INTERNATIONAL SEARCH REPORT
Information on patent family members

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Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US-A- 5112900	12/05/92	CA-A- 2055931 EP-A- 0488021 JP-A- 6025505	29/05/92 03/06/92 01/02/94
JP-A- 8120515	26/02/81	NONE	
US-A- 3933723	20/01/76	AT-B- 326909 AU-A- 5716373 BE-A- 801914 CA-A- 1038990 DE-A,C- 2333938 FR-A,B- 2236876 GB-A- 1428128 NL-A- 7309375 SE-B,C- 408558	12/01/76 09/01/75 05/11/73 19/09/78 24/01/74 16/01/75 17/03/76 08/01/74 18/06/79